FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR
215548US0XPCT	09/926510

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/02782	30 March 2000	12 May 1999

TITLE OF INVENTION

PROCESS FOR PRODUCING INHERENTLY MICROBICIDAL POLYMER SURFACES

APPLICANT(S) FOR DO/EO/US

Peter OTTERSBACH, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

PCT/IB/308
Notice of Priority
Request for Consideration of Documents Cited in the International Search Report

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/926510	PCT/EP00/02782	215548US0XPCT

24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS PTO USE ONLY
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	$1040.00	
☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	$890.00	
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	$740.00	
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	$710.00	
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =		$890.00
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).		$130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	- 20 =	0	x $18.00	$0.00
Independent claims	- 3 =	0	x $84.00	$0.00
Multiple Dependent Claims **(check if applicable)**.			☐	$0.00

TOTAL OF ABOVE CALCULATIONS =	$1,020.00
☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.	$0.00
SUBTOTAL =	$1,020.00
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +	$0.00
TOTAL NATIONAL FEE =	$1,020.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐	$0.00
TOTAL FEES ENCLOSED =	$1,020.00
Amount to be: refunded	$
charged	$

a. ☒ A check in the amount of **$1,020.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Telephone: (703)413-3000
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Surinder Sachar
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Surinder Sachar
SIGNATURE

Norman F. Oblon
NAME

24,618
REGISTRATION NUMBER

Nov. 13 2001
DATE

DOCKET NO. 215548US0XPCT

IN RE APPLICATION OF: Peter OTTERSBACH, et al.

SERIAL NO.: 09/926,510

FILED: November 13, 2001

FOR: PROCESS FOR PRODUCING INHERENTLY MICROBICIDAL POLYMER SURFACES

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

Sir:

Transmitted herewith is an amendment in the above-identified application.

☒ No additional fee is required.

☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement previously submitted.

☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement submitted herewith.

☒ Additional documents filed herewith: Preliminary Amendment/Declaration/Response to Notice Notice of Missing Requirements/Amended Sheets (Pages 2, 7,15 and 16)

The fee has been calculated as shown below.

	(Col. 1)	(Col. 2)	(Col. 3)	SMALL ENTITY		SMALL ENTITY		OTHER THAN A
	CLAIMS REMAINING AFTER		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
TOTAL	* 12	MINUS	** 20	= 0	X9 =	$	X18 =	$ .00
INDEP	* 1	MINUS	*** 3	= 0	X39=	$	X80 =	$ .00
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM					+130=	$	+270=	$
						$	TOTAL	$ .00

TOTAL

___ A check in the amount of $_____ is attached.

XX Please charge any additional fees for the papers being filed herewith and for which no check is enclosed herewith, or credit any overpayment to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

XX If these papers are not considered timely filed by the Patent and Trademark Office, then a petition is hereby made under 37 C.F.R. §1.136, and any additional fees required under 37 C.F.R. §1.136 for any necessary extension of time may be charged to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

OBLON, SPIVAK, McCLELLAND,
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*If the entry in Column 2 is less than the entry in Column 1 write "0" in Column 3.
**If the "Highest Number Previously paid for" IN THIS SPACE is less than 20 write "20" in this space.
***If the "Highest Number Previously paid for" IN THIS SPACE is less than 3 write "3" in this space.

215548US-0XPCT

#4/a

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

PETER OTTERSBACH ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: 09/926,510 :

FILED: NOVEMBER 13, 2001 :

FOR: PROCESS FOR PRODUCING INHERENTLY MICROBICIDAL POLYMER SURFACES

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please cancel Claims 8-11.

Please amend the claims as shown in the marked-up copy following this amendment to read as follows.

1. (Amended) A process for preparing an antimicrobial polymer, said process comprising

polymerizing one or more aliphatically unsaturated monomers, said one or more aliphatically unsaturated monomers at least singly functionalized by means of a tertiary amino group.

2. (Amended) The process as claimed in claim 1, wherein the one or more aliphatically unsaturated monomers are functionalized by means of a tertiary amino group of formula

$$R_1NR_2R_3$$

where R_1 is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R_2 and R_3 are identical or different and are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms.

3. (Amended) The process as claimed in Claim 1, wherein the one or more aliphatically unsaturated monomers is polymerized with one or more second aliphatically unsaturated monomers selected from the group consisting of acrylates and methacrylates.

4. (Amended) The process as claimed in Claim 1, wherein the monomers are polymerized on a substrate.

5. (Amended) The process as claimed in Claim 1, wherein the monomers are graft polymerized onto a substrate.

6. (Amended) The process as claimed in claim 5, wherein the substrate is activated prior to graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ-radiation.

7. (Amended) The process as claimed in claim 5, wherein the substrate is activated prior to graft polymerization by UV radiation with a photosensitizer.

Please add the following new claims.

12. (New) The process as claimed in Claim 3 wherein the acrylates and methacrylates are selected from the group consisting of acrylic acid, tert-butyl methacrylate, methyl methacrylate, styrene, vinyl chloride, vinyl ethers, acrylamides, acrylonitriles, allyl compounds, vinyl ketones, vinylacetic acid, vinyl acetates and vinyl esters.

13. (New) An article of manufacture comprising an antimicrobial coating, said antimicrobial coating comprising a polymer prepared by the process as claimed in Claim 1.

14. (New) A medical device comprising an antimicrobial coating, said antimicrobial coating comprising an antimicrobial polymer prepared by the process as claimed in Claim 1.

15. (New) A hygiene item comprising an antimicrobial coating, said antimicrobial coating comprising an antimicrobial polymer prepared by the process as claimed in Claim 1.

16. (New) A surface coating, protective paint or other coating comprising an antimicrobial polymer prepared by the process as claimed in Claim 1.

<u>REMARKS</u>

Claims 1-7 and 12-16 are active in the present application. Claims 8-11 have been canceled. Claims 12-16 are new claims. Support for the new claims is found in the original claims. Claims 1-7 have been amended to remove multiple dependencies and for clarity. No new matter is believed to have been added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

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Marked-Up Copy
Serial No:
09/926,570
Amendment Filed on:
2-7-02

IN THE CLAIMS

--Claims 8-11 (Canceled).

1. (Amended) A process for preparing an antimicrobial [polymers, characterized in that] polymer, said process comprising

polymerizing one or more aliphatically unsaturated monomers [which have been], said one or more aliphatically unsaturated monomers at least singly functionalized by means of a tertiary amino group [are polymerized].

2. (Amended) The process as claimed in claim 1, wherein the one or more aliphatically [characterized in that use is made of aliphatic] unsaturated monomers are functionalized by means of a tertiary amino group [and having the general] of formula

$$R_1NR_2R_3$$

where R_1 is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R_2 and R_3 are identical or different and are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms.

3. (Amended) The process as claimed in [one of claims 1 and 2, characterized in that the polymerization is carried out with other] Claim 1, wherein the one or more aliphatically unsaturated monomers is polymerized with one or more second aliphatically unsaturated monomers selected from the group consisting of acrylates and methacrylates[, for example acrylic acid, tert-butyl methacrylate, methyl methacrylate, styrene, vinyl chloride, vinyl ethers, acrylamides, acrylonitriles, allyl compounds, vinyl ketones, vinylacetic acid, vinyl acetates and vinyl esters].

4. (Amended) The process as claimed in [one of claims 1 to 3, characterized in that the polymerization is carried out] Claim 1, wherein the monomers are polymerized on a substrate.

5. (Amended) The process as claimed in [one of claims 1 to 4, characterized in that the polymerization is carried out as a graft polymerization of] Claim 1, wherein the monomers are graft polymerized onto a substrate.

6. (Amended) The process as claimed in claim 5, [characterized in that] wherein the substrate is activated prior to the graft polymerization [the substrate is activated] by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ-radiation.

7. (Amended) The process as claimed in claim 5, [characterized in that] wherein the substrate is activated prior to the graft polymerization [the substrate is activated] by UV radiation with a photosensitizer.

Claims 12-16 (New).--

CREAVIS Gesellschaft für Innovation und Technologie mbH
PATENTE ♦ MARKEN

Process for producing inherently microbicidal polymer surfaces

The invention relates to a process for preparing antimicrobial polymers by polymerizing amino-functionalized monomers, and to the use of the resultant antimicrobial polymers.

The invention further relates to a process for preparing antimicrobial polymers by graft-polymerizing amino-functionalized monomers on a substrate, and to the use of the resultant antimicrobial substrates.

It is highly undesirable for bacteria to become established or to spread on the surfaces of pipelines, containers or packaging. Frequently, slime layers form and permit sharp rises in microbial populations, and these can lead to persistent impairment of the quality of water, drinks or foods, and even to spoilage of the product and harm to the health of consumers.

Bacteria must be kept away from all areas of life in which hygiene is important. This affects textiles for direct body contact, especially in the genital area, and for the care of the elderly and sick. Bacteria must also be kept away from surfaces of furniture and instruments in wards, especially in areas for intensive care and neonatal care, in hospitals, especially in areas for medical interventions, and in isolation wards for critical cases of infection, and also in toilets.

A current method of treating equipment, or the surfaces of furniture or textiles, to resist bacteria either when this becomes necessary or else as a precautionary measure is to use chemicals or solutions or mixtures of these which as disinfectants have fairly broad general antimicrobial action. Chemical agents of this type act nonspecifically and are frequently themselves toxic or irritant, or form degradation products which are hazardous to health. In addition, people frequently exhibit intolerance to these materials once they have become sensitized.

Another method to counteract surface spread of bacteria is to incorporate

substances with antimicrobial action into a matrix.

Tert-butylaminoethyl methacrylate is a commercially available monomer in methacrylate chemistry and is used in particular as a hydrophilic constituent in copolymerizations. For example, EP 0 290 676 uses various polyacrylates and polymethacrylates as a matrix for immobilizing bactericidal quaternary ammonium compounds.

In another technical sector US-A 4 532 269 discloses a terpolymer of butyl methacrylate, tributyltin methacrylate and tert-butylaminoethyl methacrylate. This polymer is used as an antimicrobial paint for ships: the hydrophilic tert-butylaminoethyl methacrylate promotes gradual erosion of the polymer, thus liberating the highly toxic tributyltin methacrylate as antimicrobial agent.

In these applications the copolymer prepared using aminomethacrylates is merely a matrix or carrier substance for added microbicidal agents which can diffuse or migrate out of the carrier substance. Sooner or later polymers of this type lose their effectiveness once the necessary "minimal inhibitory concentration" (MIC) is no longer achieved on the surface.

European Patent Applications 0 862 858 and 0 862 859 have disclosed that homo- and copolymers of tert-butylaminoethyl methacrylate, a methacrylate having a secondary amino function, have inherent microbicidal properties. To avoid undesirable resistance phenomena in the microbes, particularly bearing in mind the development of resistance by microbes known from antibiotics research, systems developed in the future will also have to be based on novel compositions with improved effectiveness.

EP 0 331 528 discloses a process for preparing antimicrobial copolymers from ethylene and, for example, dimethylaminopropylacrylamide, where appropriate with addition of metal cations.

An object of the present invention is therefore to develop novel polymers having antimicrobial action. These, where appropriate in the form of a coating, should prevent the establishment and spread of bacteria on surfaces.

Surprisingly, it has now been found that polymerizing aliphatically unsaturated monomers which have been at least singly functionalized by

means of a tertiary amino group gives polymers with a long-lasting microbicidal surface which is not attacked by solvents or by physical stresses and which does not exhibit migration. This makes it unnecessary to use other biocides.

The present invention provides a process for preparing antimicrobial polymers, which comprises polymerizing aliphatically unsaturated monomers which have been at least singly functionalized by means of a tertiary amino group.

The aliphatically unsaturated monomers used according to the invention and at least singly functionalized by means of a tertiary amino group may have a hydrocarbon radical of up to 50 carbon atoms, preferably up to 30 carbon atoms, particularly preferably up to 22 carbon atoms. The substituents of the amino group may be aliphatic or vinylic hydrocarbon radicals, such as methyl, ethyl, propyl or acrylic radicals, or cyclic hydrocarbon radicals, such as substituted or unsubstituted phenyl or cyclohexyl radicals having up to 25 carbon atoms. The amino group may also have substitution by keto or aldehyde groups, such as acryloyl or oxo groups.

To achieve a sufficient rate of polymerization, the monomers used according to the invention should have a molar mass of less than 900, preferably less than 550 g/mol.

A particular embodiment of the present invention uses aliphatic unsaturated monomers singly functionalized by means of a tertiary amino group and having the general formula

$$R^1NR^2R^3$$

where R^1 is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R^2 and R^3 are identical or different and are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms.

Suitable monomeric building blocks are aliphatically unsaturated monomers which have at least one tertiary amino function, e.g. 2-diethylaminoethyl methacrylate, 2-dimethylaminoethyl methacrylate, 3-dimethylamino-propylmethacrylamide, 2-diethylaminoethyl acrylate, 2-dimethylaminoethyl acrylate, 3-dimethylaminopropyl acrylate or 3-dimethylamino-2,2-dimethylpropyl acrylate.

The novel process may also be carried out by polymerizing the monomers at least singly functionalized by means of a tertiary amino group on a substrate. This gives a physisorbed coating of the antimicrobial polymer on the substrate.

Suitable substrate materials are especially any of the polymeric plastics, such as polyurethanes, polyamides, polyesters and polyethers, polyether block amides, polystyrene, polyvinyl chloride, polycarbonates, polyorganosiloxanes, polyolefins, polysulfones, polyisoprene, polychloroprene, polytetrafluoroethylene (PTFE) or corresponding copolymers or blends, or also naturally occurring or synthetic rubbers, with or without radiation-sensitive groups. The novel process may also be used on surfaces of objects made from metal, from glass or from wood and surface-coated or otherwise coated with plastic.

In another embodiment of the present invention the antimicrobial polymers may be obtained by graft-polymerizing a substrate with an aliphatically unsaturated monomer at least singly functionalized by means of a tertiary amino group. The grafting of the substrate allows covalent linking of the antimicrobial polymer to the substrate. Substrates which may be used are any polymeric material, such as the plastics mentioned above.

Prior to the graft polymerization, the surfaces of the substrate may be activated by a variety of methods. Any standard method for activating polymer surfaces may be used here, for example the substrate may be activated prior to the graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ-radiation. The surfaces are usefully freed in advance in a known manner from oils, fats or other contamination, using a solvent.

The substrate may be activated by UV radiation in the wavelength range from 170 to 400 nm, preferably from 170 to 250 nm. An example of a suitable radiation source is a Noblelight UV excimer apparatus from HERAEUS, Hanau, Germany. However, mercury vapor lamps are also suitable for substrate activation as long as they emit substantial proportions of radiation in the abovementioned ranges. The exposure time is generally from 0.1 second to 20 minutes, preferably from 1 second to 10 minutes.

The activation of the standard polymers with UV radiation may moreover also use a photosensitizer. For this, the photosensitizer, such as benzophenone, is applied to the substrate surface and irradiated. A mercury vapor lamp may again be used here, with exposure times of from 0.1 second to 20 minutes, preferably from 1 second to 10 minutes.

According to the invention, the activation may also be achieved by plasma treatment using an RF or microwave plasma (Hexagon, Technics Plasma, 85551 Kirchheim, Germany) in air, nitrogen or argon atmospheres. The exposure times are generally from 2 seconds to 30 minutes, preferably from 5 seconds to 10 minutes. The energy supplied in the case of laboratory devices is from 100 to 500 W, preferably from 200 to 300 W.

Corona devices (SOFTAL, Hamburg, Germany) may also be used for activation. The exposure times in this case are generally from 1 to 10 minutes, preferably from 1 to 60 seconds.

Activation by electrical discharge, electron beam or γ-radiation (e.g. from a

cobalt 60 source), and also ozonization, allow short exposure times, generally from 0.1 to 60 seconds.

Substrate surfaces may also be activated by flame treatment. Suitable devices, in particular those with a barrier flame front, can readily be constructed or, for example, purchased from ARCOTEC, 71297 Mönsheim, Germany. They may be operated using hydrocarbons or hydrogen as combustion gas. In all cases it is necessary to avoid damage to the substrate by overheating, and this can readily be ensured if the substrate surface facing away from the flame treatment side is in intimate contact with a cooled metal surface. Activation by flame treatment is therefore restricted to relatively thin, sheet-like substrates. The exposure times are generally from 0.1 second to 1 minute, preferably from 0.5 to 2 seconds. The flames are exclusively nonluminous, and the distances between the substrate surfaces and the outer side of the flame front are from 0.2 to 5 cm, preferably from 0.5 to 2 cm.

The substrate surfaces activated in this way are coated by known methods, such as dipping, spraying or spreading, with aliphatically unsaturated monomers which have been at least singly functionalized by means of a tertiary amino group, where appropriate in solution. Solvents which have proven useful are water and water/ethanol mixtures, but other solvents may also be used as long as they are sufficiently capable of dissolving the monomers and give good wetting of the substrate surfaces. Examples of other solvents are ethanol, methanol, methyl ethyl ketone, diethyl ether, dioxane, hexane, heptane, benzene, toluene, chloroform, dichloromethane, tetrahydrofuran and acetonitrile. Solutions with monomer contents of from 1 to 10% by weight, for example about 5% by weight, have proven successful in practice and generally give, in a single pass, coherent coatings which cover the substrate surface and have thicknesses which can be more then 0.1 µm.

The graft polymerization of the monomers applied to the activated surfaces may usefully be initiated by radiation in the short-wave segment of the visible range or in the long-wave segment of the UV range of electromagnetic

"Amended page"

radiation. For example, the radiation from a UV excimer of wavelengths from 250 to 500 nm, preferably from 290 to 320 nm, is very suitable. Mercury vapor lamps are also suitable here as long as they emit substantial proportions of radiation in the abovementioned ranges. The exposure times are generally from 10 seconds to 30 minutes, preferably from 2 to 15 minutes.

A graft polymerization may also be achieved by a process described in European Patent Application 0 872 512, based on a graft polymerization of monomer molecules and initiator molecules incorporated by a swelling process.

Other aliphatically unsaturated monomers may be used in the novel process besides the monomers functionalized by means of a tertiary amino group. For example, the monomer mixture used may comprise an aliphatically unsaturated monomer at least singly functionalized by means of a tertiary amino group together with acrylates or methacrylates, for example acrylic acid, tert-butyl methacrylate or methyl methacrylate, styrene, vinyl chloride, vinyl ethers, acrylamides, acrylonitriles, allyl compounds, vinyl ketones, vinylacetic acid, vinyl acetates or vinyl esters.

The antimicrobial polymers prepared by the novel process from aliphatically unsaturated monomers which have been at least singly functionalized by means of a tertiary amino group exhibit microbicidal or antimicrobial behavior even without grafting onto a substrate surface.

If the novel process is used directly on the substrate surface without grafting, conventional free-radical initiators may be added. Examples of initiators which may be used are azonitriles, alkyl peroxides, hydroperoxides, acyl peroxides, peroxoketones, peresters, peroxocarbonates, peroxodisulfate, persulfate and any of the usual photoinitiators, such as acetophenones, α-hydroxyketones, dimethylketals and benzophenone. The polymerization may also be initiated thermally or, as already stated, by electromagnetic radiation, such as UV light or γ-radiation.

Use of the modified polymer substrates

The present invention also provides the use of the antimicrobial polymers prepared according to the invention for producing antimicrobially active products, and the products per se which are produced in this way. The products may comprise polymer substrates modified according to the invention or consist of these. Products of this type are preferably based on polyamides, polyurethanes, polyether block amides, polyesteramides or -imides, PVC, polyolefins, silicones, polysiloxanes, polymethacrylate or polyterephthalates surface-modified using novel polymers.

Examples of antimicrobially active products of this type are in particular machine parts for processing food and drink, components in air-conditioning systems, roofing, items for bathroom and toilet use, kitchen items, components of sanitary equipment, components of cages or houses for animals, recreational products for children, components of water systems, packaging for food or drink, operator units (touch panels) of devices, and contact lenses.

The novel polymers or graft copolymers may be used anywhere where importance is placed on surfaces with release properties or surfaces which are as free as possible from bacteria, i.e. microbicidal. Examples of application of the novel polymers or graft polymers are in particular surface coatings, protective paints and other coatings in the following sectors:

Marine: Boat hulls, docks, buoys, drilling platforms, ballast water tanks

Construction: Roofing, basements, walls, facades, greenhouses, sun protection, garden fencing, wood protection

Sanitary: Public conveniences, bathrooms, shower curtains, toilet items, swimming pool, sauna, jointing, sealing compounds

- Requisites for daily life: Machines, kitchen, kitchen items, sponge pads, recreational products for children, packaging for food or drink, milk processing, drinking water systems, cosmetics

Machine parts: Air-conditioning systems, ion exchangers, process water, solar-powered units, heat exchangers, bioreactors, membranes

Medical technology: Contact lenses, diapers, membranes, implants

Consumer articles: Automobile seats, clothing (socks, sport clothing), hospital equipment, door handles, telephone handsets, public conveyances, animal cages, cash registers, wall-to-wall carpets, wallpapers.

The present invention also provides the use of the polymer substrates surface-modified using antimicrobial polymers prepared according to the invention for producing hygiene products or items for medical technology. That which has been said above concerning preferred materials applies correspondingly. Examples of hygiene products of this type are toothbrushes, toilet seats, combs and packaging materials. The term hygiene items also includes other objects which may come into contact with a large number of people, such as telephone handsets, stair rails, door handles, window catches, and also grab straps and grab handles in public conveyances. Examples of items for medical technology are catheters, tubing, protective or backing films and surgical instruments.

The following examples are given in order to describe the present invention in greater detail, but are not intended to limit its scope as set out in the claims.

Example 1:

A nylon-12 film is exposed for 2 minutes at a pressure of 1 mbar to 172 nm radiation from a Heraeus excimer source. The film activated in this way is placed into an irradiator under an inert gas and secured. Under a counterstream of inert gas the film is then covered with 20 ml of a mixture of 3 g of 2-diethylaminoethyl methacrylate (Aldrich) and 97 g of methanol. The irradiation chamber is sealed and placed at a distance of 10 cm from a Heraeus excimer source emitting at wavelength 308 nm. Irradiation is begun and continues for 15 minutes. The film is then removed and rinsed with 30 ml of methanol, then dried for 12 hours at 50°C in vacuo, then extracted 5 times with water for 6 hours at 30°C, and then dried at 50°C for 12 hours.

The reverse side of the film is then treated in the same way so that the polyamide film finally obtained has been coated on both sides with grafted polymer.

Example 1a:

A piece of coated film from Example 1 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus aureus microbes are now detectable.

Example 1b:

A piece of coated film from Example 1 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has fallen from 10^7 to 10^4.

Example 2:

A nylon-12 film is exposed for 2 minutes at a pressure of 1 mbar to 172 nm radiation from a Heraeus excimer source. The film activated in this way is placed into an irradiator under an inert gas and secured. Under a counterstream of inert gas the film is then covered with 20 ml of a mixture of 3 g of N-(3-dimethylaminopropyl)meth-acrylamide (Aldrich) and 97 g of methanol. The irradiation chamber is sealed and placed at a distance of 10 cm from a Heraeus excimer source emitting at wavelength 308 nm. Irradiation is begun and continues for 15 minutes. The film is then removed and rinsed with 30 ml of methanol, then dried for 12 hours at 50°C in vacuo, then extracted 5 times with water for 6 hours at 30°C, and then dried at 50°C for 12 hours.

The reverse side of the film is then treated in the same way, so that the polyamide film finally obtained has been coated on both sides with grafted polymer.

Example 2a:

A piece of coated film from Example 2 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed and the number of

microbes in the test mixture is determined. After expiry of this time no Staphylococcus aureus microbes are now detectable.

Example 2b:

A piece of coated film from Example 2 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has fallen from 10^7 to 10^4.

Example 3:

A nylon-12 film is exposed for 2 minutes at a pressure of 1 mbar to 172 nm radiation from a Heraeus excimer source. The film activated in this way is placed into an irradiator under an inert gas and secured. Under a counterstream of inert gas the film is then covered with 20 ml of a mixture of 3 g of 3-dimethylaminopropyl acrylate (Aldrich) and 97 g of methanol. The irradiation chamber is sealed and placed at a distance of 10 cm from a Heraeus excimer source emitting at wavelength 308 nm. Irradiation is begun and continues for 15 minutes. The film is then removed and rinsed with 30 ml of methanol, then dried for 12 hours at 50°C in vacuo, then extracted 5 times with water for 6 hours at 30°C, and then dried at 50°C for 12 hours.
The reverse side of the film is then treated in the same way so that the polyamide film finally obtained has been coated on both sides with grafted polymer.

Example 3a:

A piece of coated film from Example 3 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus aureus microbes are now detectable.

Example 3b:

A piece of coated film from Example 3 (5 x 4 cm) is shaken in 30 ml of a test

microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has fallen from 10^7 to 10^3.

Example 4:

A nylon-12 film is exposed for 2 minutes at a pressure of 1 mbar to 172 nm radiation from a Heraeus excimer source. The film activated in this way is placed into an irradiator under an inert gas and secured. Under a counterstream of inert gas the film is then covered with 20 ml of a mixture of 3 g of 2-diethylaminoethyl methacrylate (Aldrich), 2 g of methylmethacrylate (Aldrich) and 95 g of methanol. The irradiation chamber is sealed and placed at a distance of 10 cm from a Heraeus excimer source emitting at wavelength 308 nm. Irradiation is begun and continues for 15 minutes. The film is then removed and rinsed with 30 ml of methanol, then dried for 12 hours at 50°C in vacuo, then extracted 5 times with water for 6 hours at 30°C, and then dried at 50°C for 12 hours.

The reverse side of the film is then treated in the same way so that the polyamide film finally obtained has been coated on both sides with grafted polymer.

Example 4a:

A piece of coated film from Example 4 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus aureus microbes are now detectable.

Example 4b:

A piece of coated film from Example 4 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has fallen from 10^7 to 10^3.

Example 5:

A nylon-12 film is exposed for 2 minutes at a pressure of 1 mbar to 172 nm radiation from a Heraeus excimer source. The film activated in this way is placed into an irradiator under an inert gas and secured. Under a counterstream of inert gas the film is then covered with 20 ml of a mixture of 3 g of N-(3-dimethylaminopropyl)meth-acrylamide (Aldrich), 2 g of methyl methacrylate (Aldrich) and 95 g of methanol. The irradiation chamber is sealed and placed at a distance of 10 cm from a Heraeus excimer source emitting at wavelength 308 nm. Irradiation is begun and continues for 15 minutes. The film is then removed and rinsed with 30 ml of methanol, then dried for 12 hours at 50°C in vacuo, then extracted 5 times with water for 6 hours at 30°C, and then dried at 50°C for 12 hours.

The reverse side of the film is then treated in the same way, so that the polyamide film finally obtained has been coated on both sides with grafted polymer.

Example 5a:

A piece of coated film from Example 5 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus aureus microbes are now detectable.

Example 5b:

A piece of coated film from Example 5 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has fallen from 10^7 to 10^4.

In addition to the microbicidal action described above with respect to cells of Pseudomonas aeruginosa and Staphylococcus aureus, all of the specimens also exhibited microbicidal action with respect to cells of Klebsiella

pneumoniae, Escherichia coli, Rhizopus oryzae, Candida tropicalis and Tetrahymena pyriformis.

Patent claims:

1. A process for preparing antimicrobial polymers,
characterized in that
aliphatically unsaturated monomers which have been at least singly functionalized by means of a tertiary amino group are polymerized.

2. The process as claimed in claim 1,
characterized in that
use is made of aliphatic unsaturated monomers functionalized by means of a tertiary amino group and having the general formula

$$R_1NR_2R_3$$

where R_1 is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R_2 and R_3 are identical or different and are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms.

3. The process as claimed in one of claims 1 and 2,
characterized in that
the polymerization is carried out with other aliphatically unsaturated monomers selected from the group consisting of acrylates and methacrylates, for example acrylic acid, tert-butyl methacrylate or methyl methacrylate, styrene, vinyl chloride, vinyl ethers, acrylamides, acrylonitriles, allyl compounds, vinyl ketones, vinylacetic acid, vinyl acetates and vinyl esters.

4. The process as claimed in one of claims 1 to 3,
characterized in that
the polymerization is carried out on a substrate.

5. The process as claimed in one of claims 1 to 4,
characterized in that
the polymerization is carried out as a graft polymerization of a substrate.

6. The process as claimed in claim 5,

characterized in that
prior to the graft polymerization the substrate is activated by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ-radiation.

7. The process as claimed in claim 5,
characterized in that
prior to graft polymerization the substrate is activated by UV radiation with a photosensitizer.

8. The use of antimicrobial polymers prepared as claimed in one of claims 1 to 7 for producing products with an antimicrobial coating of the polymer.

9. The use of antimicrobial polymers prepared as claimed in one of claims 1 to 7 for producing items for medical technology with an antimicrobial coating of the polymer.

10. The use of antimicrobial polymers prepared as claimed in one of claims 1 to 7 for producing hygiene items with an antimicrobial coating of the polymer.

11. The use of antimicrobial polymers prepared as claimed in one of claims 1 to 7 for producing surface coatings, protective paints or other coatings.

#3

Declaration and Power of Attorney for Patent Application
Erklärung für Patentanmeldungen mit Vollmacht

German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides Statt:

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As a below named inventor, I hereby declare that:

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I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR PRODUCING INHERENTLY

MICROBICIDAL POLYMER SURFACES

_____

the specification of which

☐ is attached hereto

☒ XX was filed on March 30, 2000

as United States Application Number or PCT International Application Number

PCT/EP00/02782

_____ and was amended on

_____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

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Prior foreign application(s)
(Frühere ausländische Anmeldungen)

(Number) (Nummer)	(Country) (Land)	(Day/Month/Year Filed) (Tag/Monat/Jahr der Anmeldung)	Priority claimed / Priorität beansprucht: Yes Ja	No Nein
199 21 897.8	GERMANY	May 12, 1999	XX	☐
			☐	☐

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(Application No.) (Aktenzeichen)	(Filing Date) (Anmeldetag)	(Status) (patented, pending, abandoned) (Status) (patentiert, schwebend, aufgegeben)
PCT/EP00/02782	March 30, 2000	pending

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POWER OF ATTORNEY As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith *(list name and registration number)*

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